CN:2121109035

Enhancement of Resist Performance by Proton Source Unit on Polymer Bound PAG Platform

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Looking Ahead with New Technologies Looking Ahead with New Technologies Looking Ahead with New Technologies Looking Ahead with New Technologies Looking Ahead with New Technologies Looking Ahead with New Technologies

EUVL Symposium on October 17, 2011, Miami, USA

To overcome the RLS Trade-off Relationship for EUV resist

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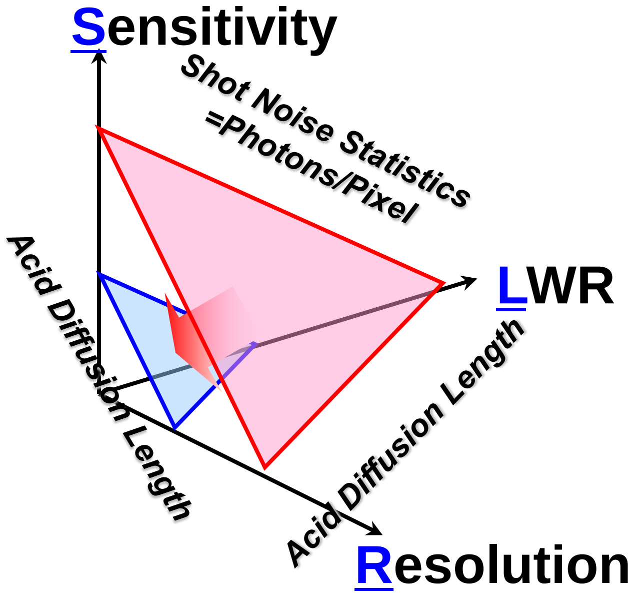
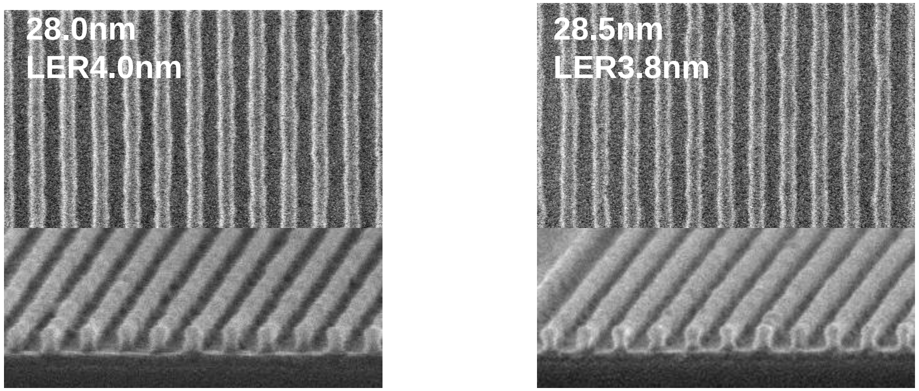


D.Van Steenwinckel et al.,
Proc. SPIE, 5753, 269-280 (2005)

Blend PAG
28nmLS Eop : 16.4mJ/cm²
Z-factor : 5.76E-08 (mJ·nm³)

Polymer Bound PAG
28nmLS Eop : 17.5mJ/cm²
Z-factor : 5.55E-08 (mJ·nm³)



- **Polymer bound PAG looks very promising especially from acid diffusion point of view in order to achieve high resolution, however extremely suppressed acid diffusion results in slower sensitivity. This is RLS trade-off.**
- **To overcome this trade-off, it's needed to consider to breakthrough it.**
- **Not only Polymer Bound PAG but also other functions are needed to overcome the RLS trade-off.**

To overcome the RLS Trade-off Relationship for EUV resist

Stochastic simulation of EUV resist

Effect of increasing the resist quantum yield

13.5 nm, 0.25 NA, 0.5 sigma, 30 nm L/SP , 18 mJ/cm2

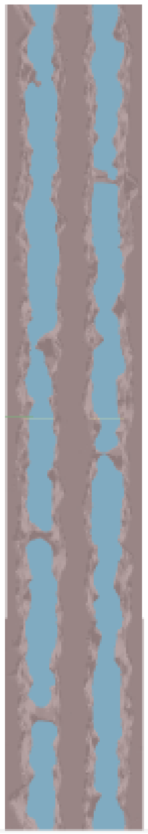
Data courtesy of John J. Biafore of KLA-Tencor

$18\,mJ/cm^2$

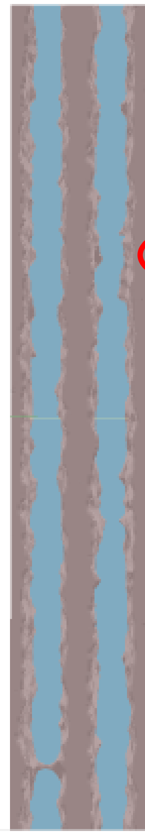
$\langle CD \rangle = 30.2\,nm$

$\boxed{LWR = 5.5\,nm}$

$\Phi = 1.0$



Increase Φ



$18\,mJ/cm^2$

$\langle CD \rangle = 29.7\,nm$

$\boxed{LWR = 4.5\,nm}$

$\Phi = 3.0$

$$\Phi = \frac{\langle n\ Acids \rangle}{\langle n\ Photons \rangle}$$

$$\text{relative uncertainty} = \frac{\sigma_{nAcids}}{\langle n\ Acids \rangle} \equiv \frac{\sigma_{n\ Acids}}{\langle n_{photons} \rangle \Phi}$$

- Higher quantum yield results in less relative uncertainty in the # of acids

■**Higher Acid yield contribute lower LWR.**

■**To overcome RLS trade-off relationship, higher Acid yield could be key word.**

Acid generation mechanism on EUV Lithography

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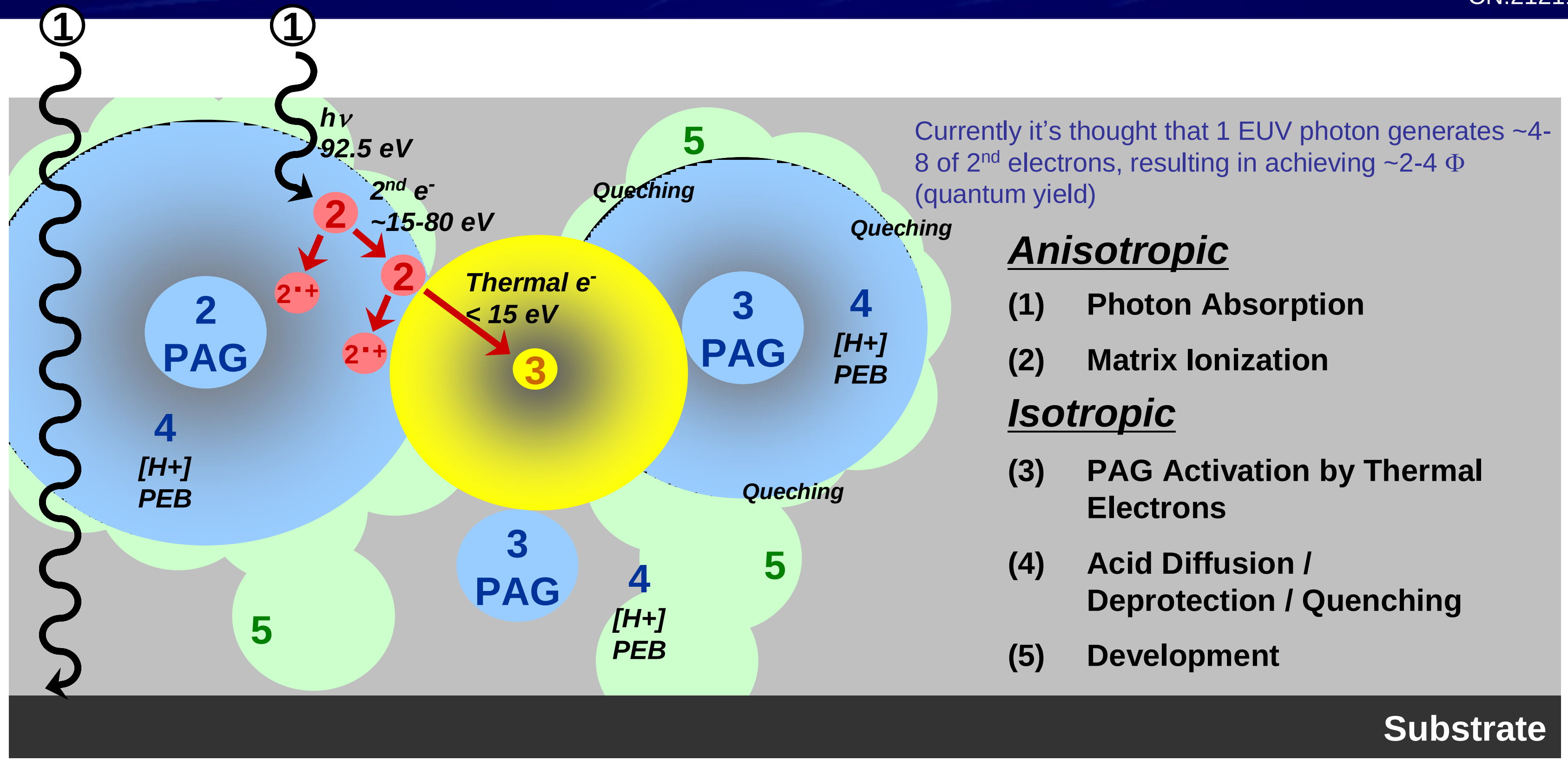

Currently it's thought that 1 EUV photon generates ~4-8 of 2nd electrons, resulting in achieving ~2-4 Φ (quantum yield)

Anisotropic

(1) Photon Absorption

(2) Matrix Ionization

Isotropic

(3) PAG Activation by Thermal Electrons

(4) Acid Diffusion / Deprotection / Quenching

(5) Development

Tagawa, Kozawa, Gallatin, Brainard, Fedynyshyn, etc.
Courtesy of Todd R. Younkin

- **Step1:** **Polymer+*hv* (13.5nm) → $(\text{Polymer})^{\cdot+}$ + e^-**
- **Step2:** **$(\text{Polymer})^{\cdot+}$ → deprotonation (H^+)**
- **Step3:** **e^- + PAG → Fragment + Counter Anion$^-$**
- **Step4:** **H^+ + Counter Anion$^-$ → Acid**

■Proton should be provided from polymer matrix at EUVL.

How to increase amount of generated acids

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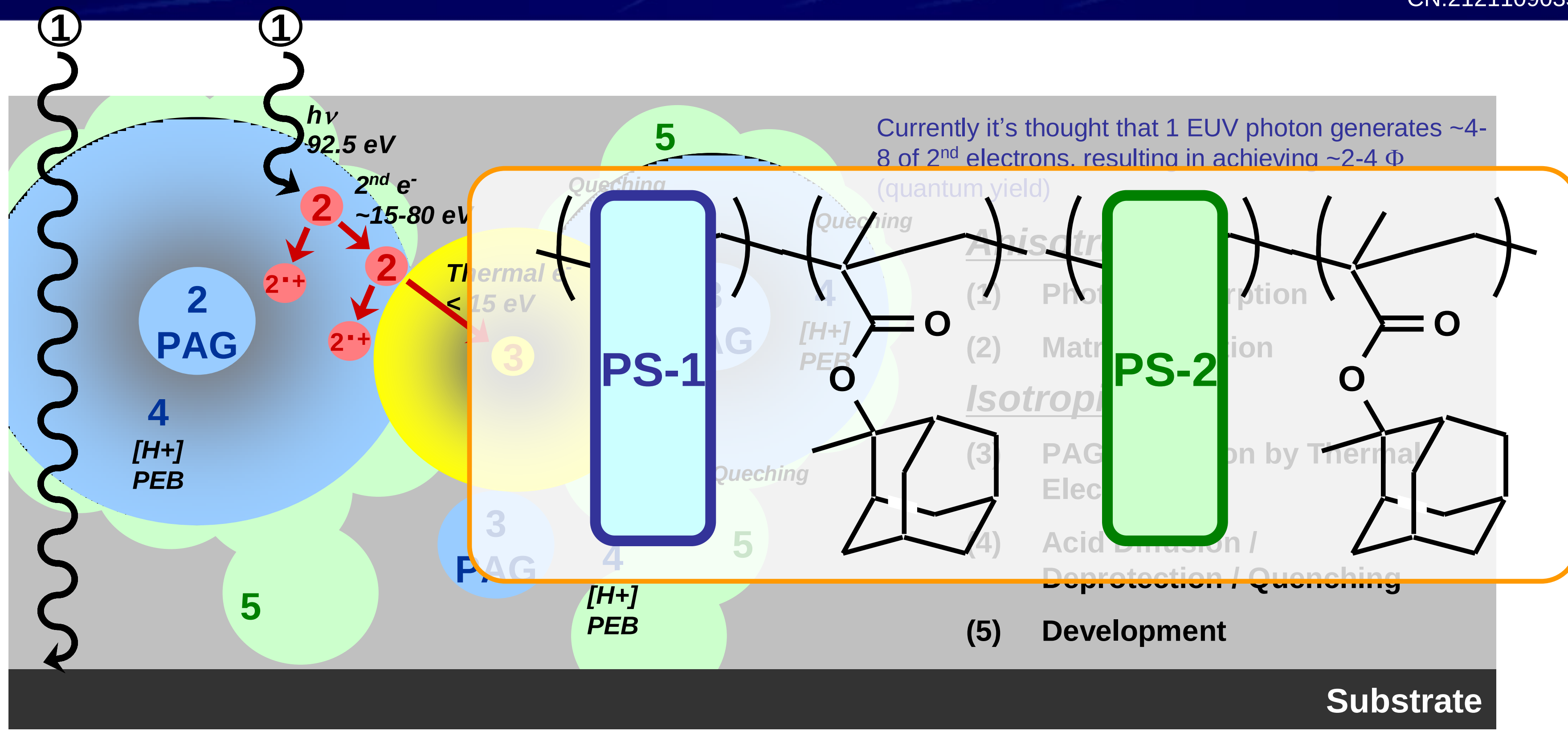

Tagawa, Kozawa, Gallatin, Brainard, Fedynyshyn, etc.
Courtesy of Todd R. Younkin

- **Increasing number of secondary electron → introducing fluorine atom into polymer**
  - ✓ T.Kozawa et al., Jpn. J. Appl. Phys. 47 (2008) 8328.
- **Increasing electron affinity of the PAG cation**
  - ✓ S. Masuda et al., Proc. SPIE 6153 (2006) 615342.
  - ✓ Yoshiyuki Utsumi et al., Jpn. J. Appl. Phys. 48 (2009).
- **Giving proton source such as phenol group into polymer matrix for acid generation**
  - ✓ H. Yamamoto et al., Jpn. J. Appl. Phys. 43 (2004) 3971.
  - ✓ H. Yamamoto et al., Jpn. J. Appl. Phys. 46 (2007) L142.

To investigate the Acid yield

If our proton source candidates can work as expected, the sensitivity must be getting faster. And in order to consider how the sensitivity is improved, we have to think about several factors as you can see here.

- **PAG and quencher loading ratio.**
  → Those are basically fixed to be no change.
- **Resist Tg** TF method : M. Irie et al.,Proc SPIE, 6923, 692310 (2008)
- **Proton source unit**
- **Etc..**

Contents

- **Generated acid measurement**
- **Sensitivity investigation on EB and EUV exposure**
- **Relationship between resist T*g* and E0 sensitivity**
- **EUV exposure results of polymer bound PAG with proton source unit**

Measurement of generated acid amount

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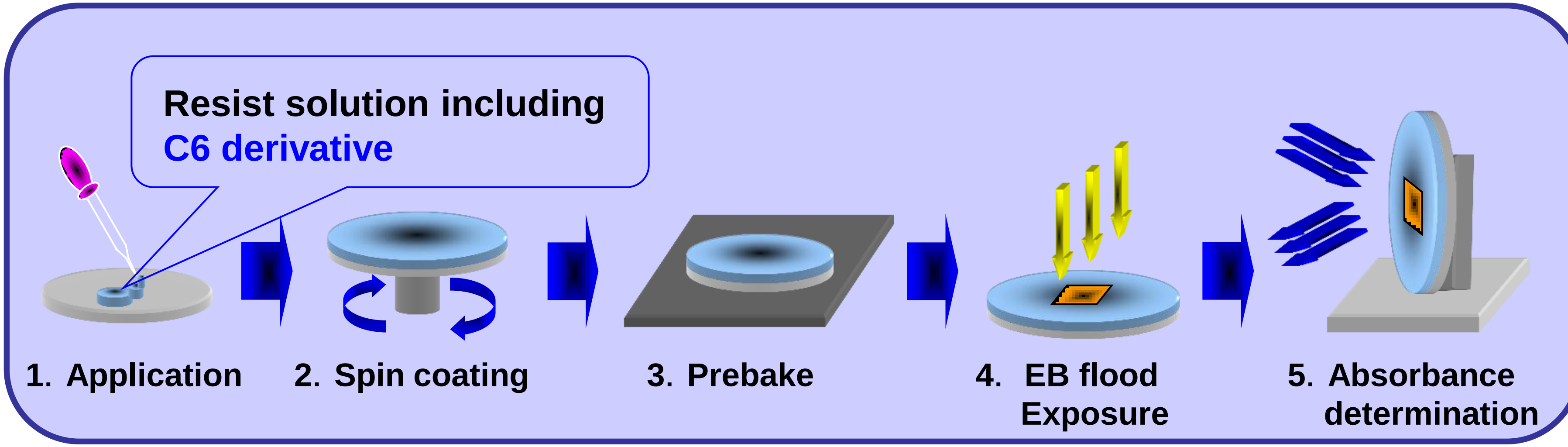
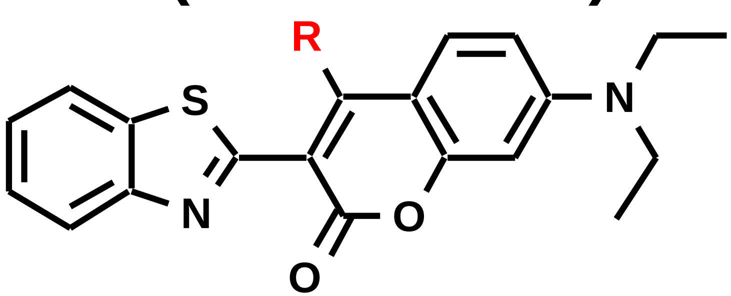


Coumarin 6 derivative
(C6 derivative)



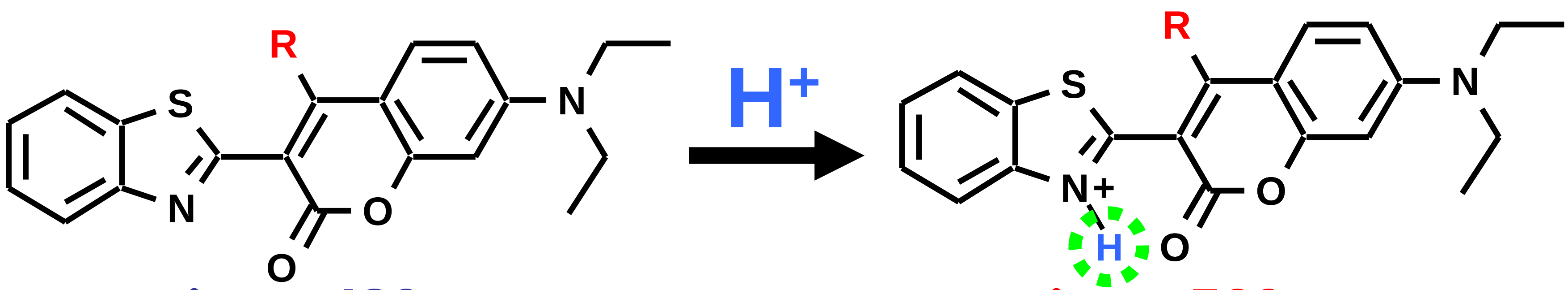
- Coumarin 6 is one of the acid indicator.
- R unit is substituted to enhance of solubility for resist solvent.

R. Hirose et al.,Proc SPIE, 6923 (2008) 69232A
C. T. Lee et al.,Proc SPIE, 6923 (2008) 69232F

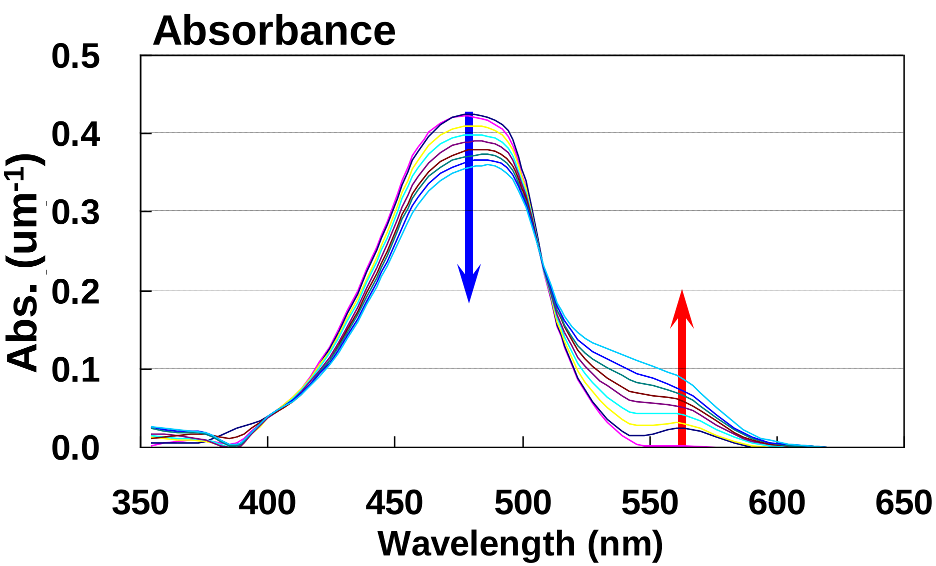
Measurement of generated acid amount
- Absorption spectra change -

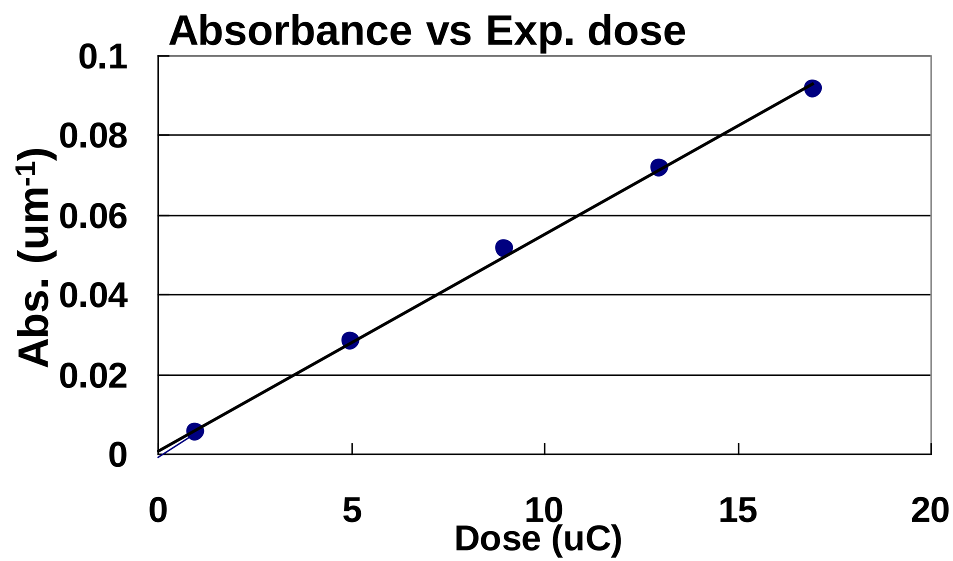
C6 derivative

R. Hirose et al.,Proc SPIE, 6923 (2008) 69232A
C. T. Lee et al.,Proc SPIE, 6923 (2008) 69232F



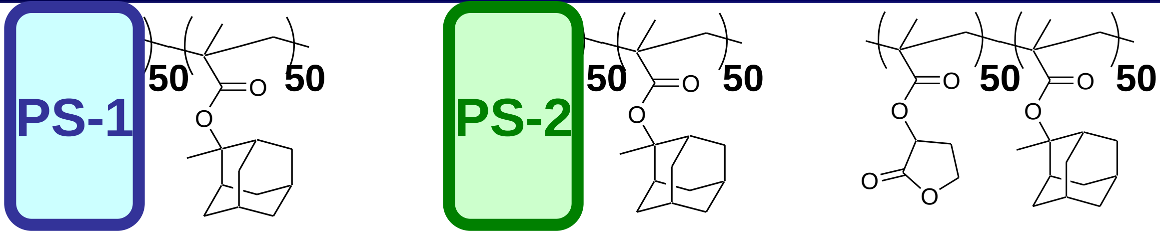
λ_{max}~480 nm λ_{max}~560 nm





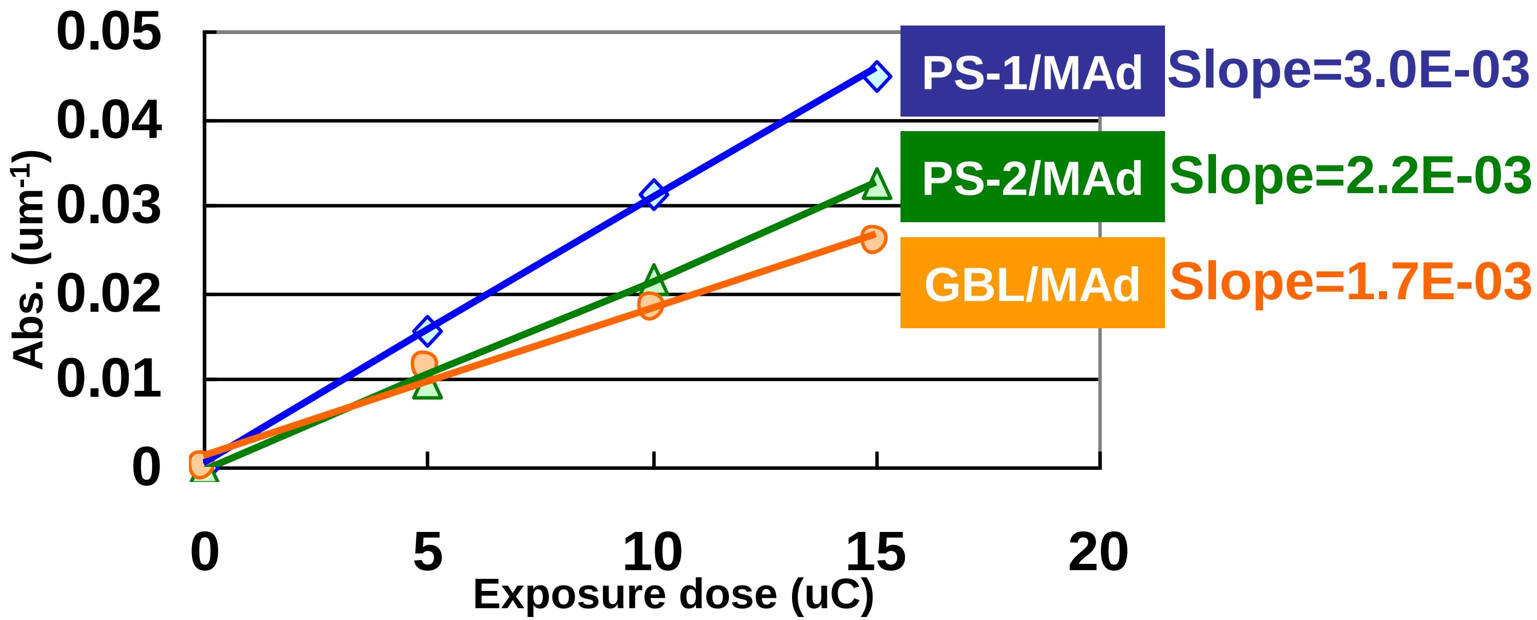
- **Absorption spectra changes with increased dose.**

Generated acid amount during exposure



PS-1/MAd PS-2/MAd GBL/MAd

Exposure
Substrate: Si
Thickness: 300nm
PAB: 90℃/120s
Exposure tool: EBeam 70kV
Ellipsometry
Wavelength: 295nm to 1033nm



- **Steeper slope means that larger amount of acid is generated.**
- **PS-1 and PS-2 can work as a better proton source than GBL/MAd with larger amount of acid.**

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- Generated acid measurement
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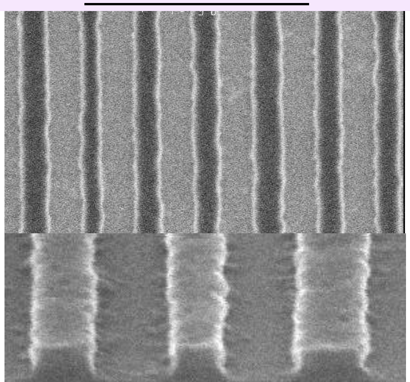
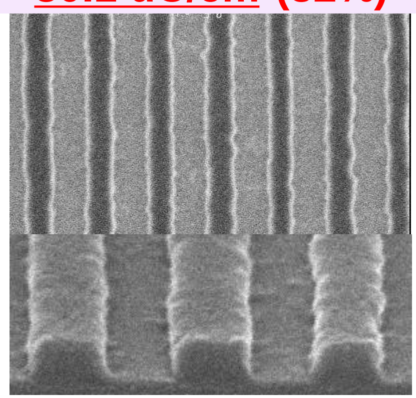
EB prescreening
- Make the resist consisting Proton Source -

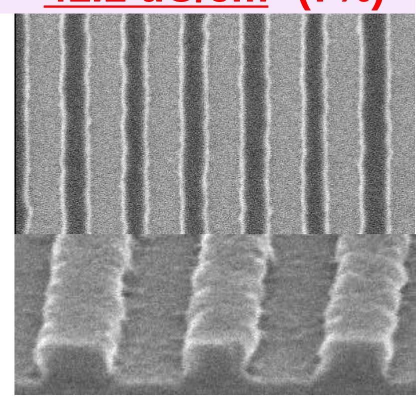
- Three samples were evaluated in order to check the effectiveness of proton source unit.
- TEST PS-1 shows 32% higher sensitivity than control.
- For the resist consisting of PS-1 unit, quencher loading ratio can be increased to fit the dose-to-size.

Sample	Control	TEST PS-1	TEST PS-2
PAB/PEB	110/90	110/90	110/90
Quencher	**1.0 eq.**	**1.0 eq.**	**1.0 eq.**
LER	6.20 nm	8.15 nm	7.56 nm
EL ±10%	26.19%	27.16%	25.97%
Esize	44.4 uC/cm^2	30.1 uC/cm^2(32%)	41.1 uC/cm^2 (7%)

100nm L/S optimum







Effectiveness of Proton Source unit

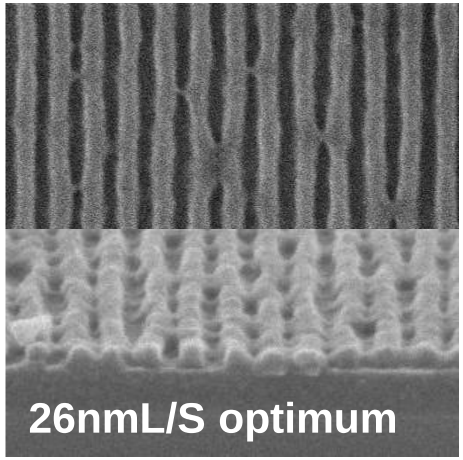
- Albany MET result with Quadrupole illumination -

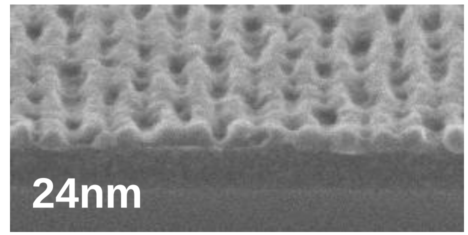
Z-factor (mJ*nm3)
= (Resolution)^3 x (LER)^2 x Sensitivity

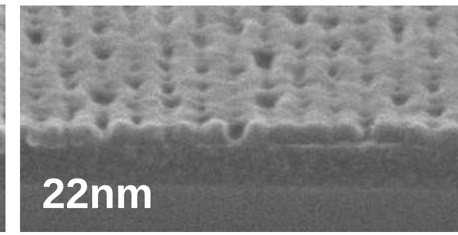
T. Wallow et al., Proc. SPIE, 6921, 69211F (2008)

Blend Control

Quencher: 1.0eq
Eop: 19.95mJ/cm^2
LWR:6.4nm
Z-factor
7.18E-08 (mJ·nm^3)

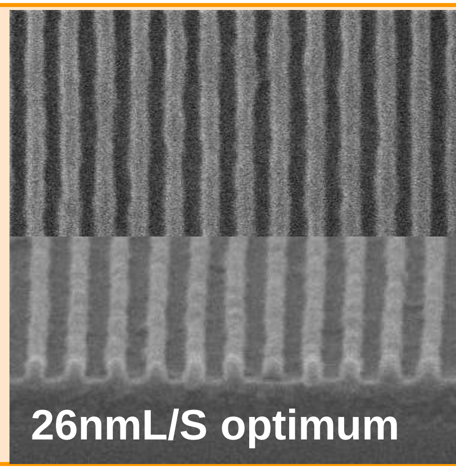


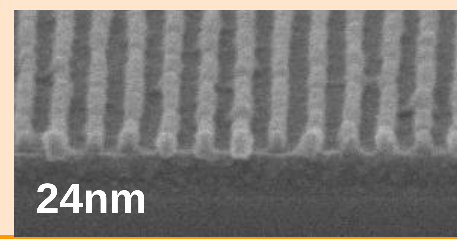


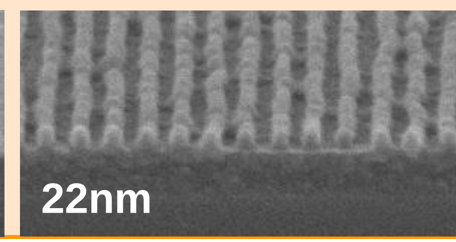


Blend w/ PS-1

Quencher: 1.5eq
Eop: 15.7mJ/cm^2
LWR:5.9nm
Z-factor
4.80E-08 (mJ·nm^3)



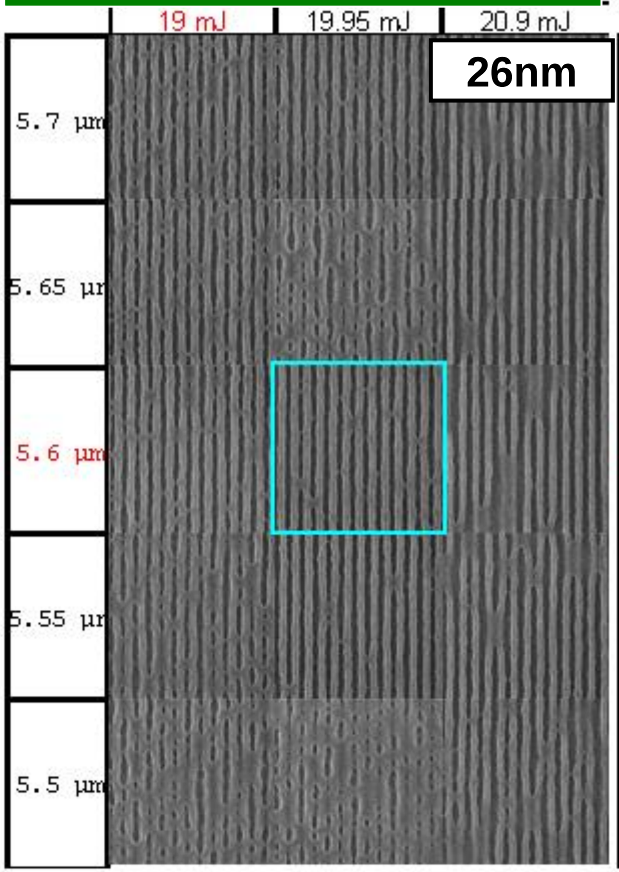


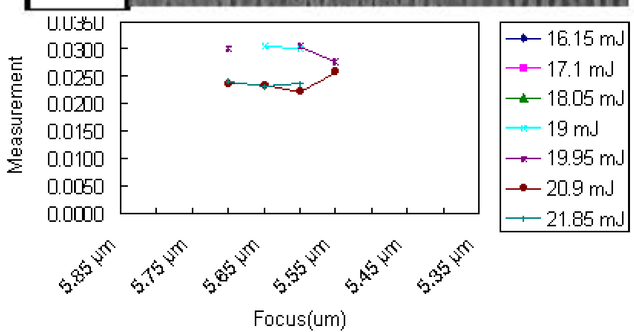


- **The sensitivity of both of the samples was set to be similar by adjusting quencher loading ratio on the basis of EB prescreening. And those resists consist of the same PAG in same loading ratio.**
- **From MET exposure results, modified PS-1 resist shows better sensitivity and roughness resulting in better Z-factor.**

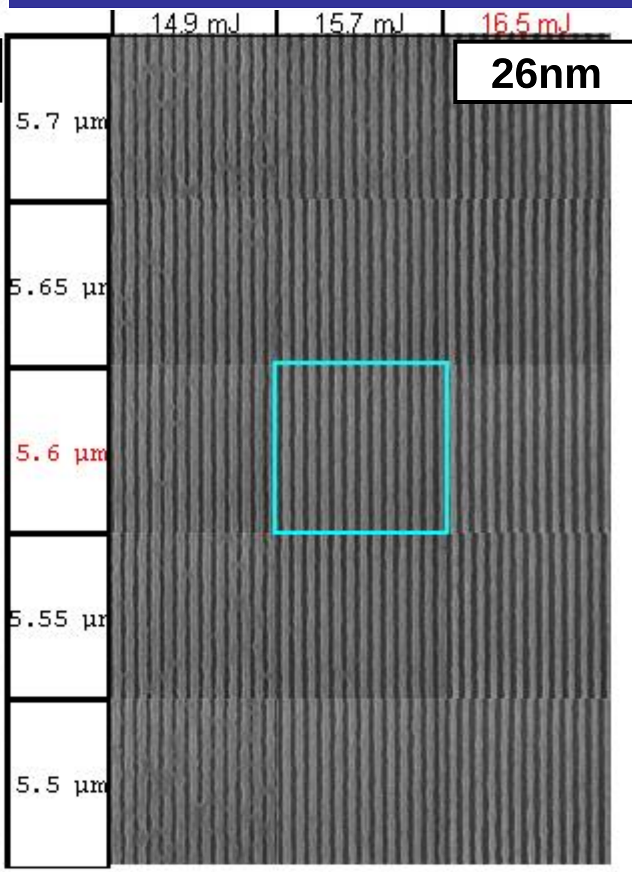
Effectiveness of Proton Source unit - FEM data -

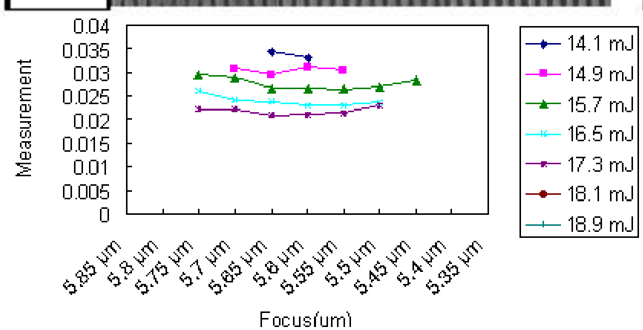
Blend Control
Eop: 19.95mJ/cm²

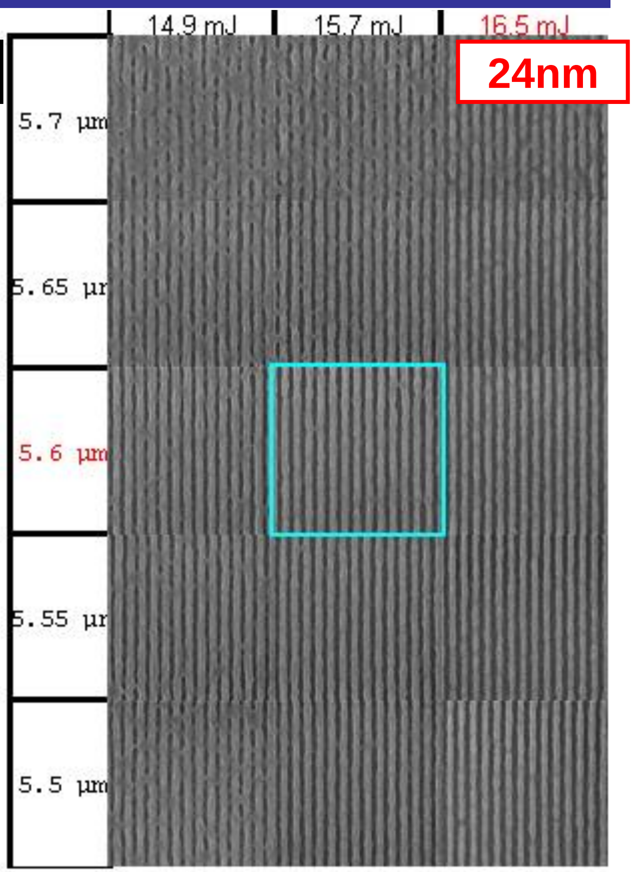


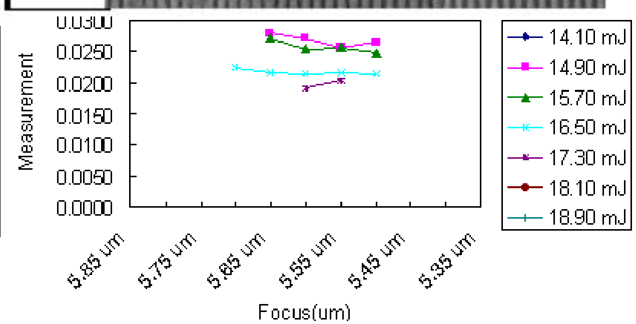


Blend w/ PS-1
Eop: 15.7mJ/cm²









Contents

- Generated acid measurement
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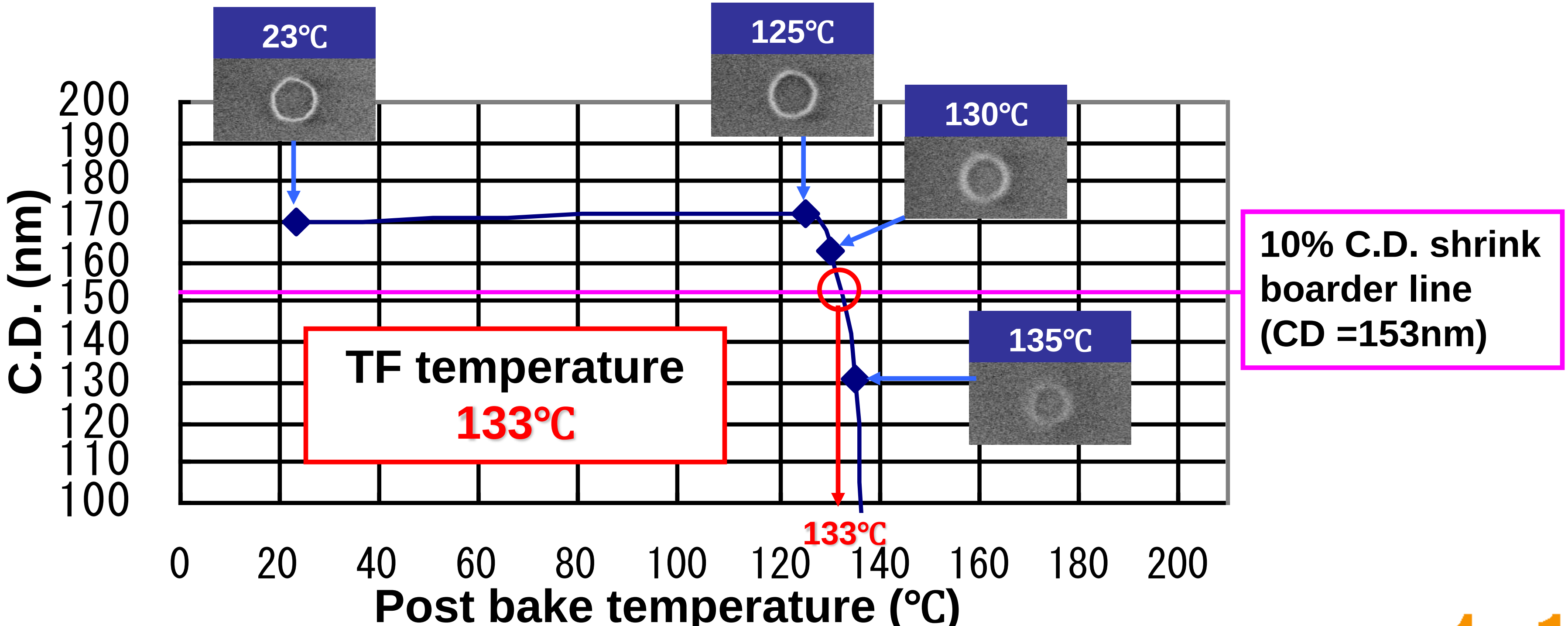
Measurement of Thermal Flow temperature

- **Process flow**

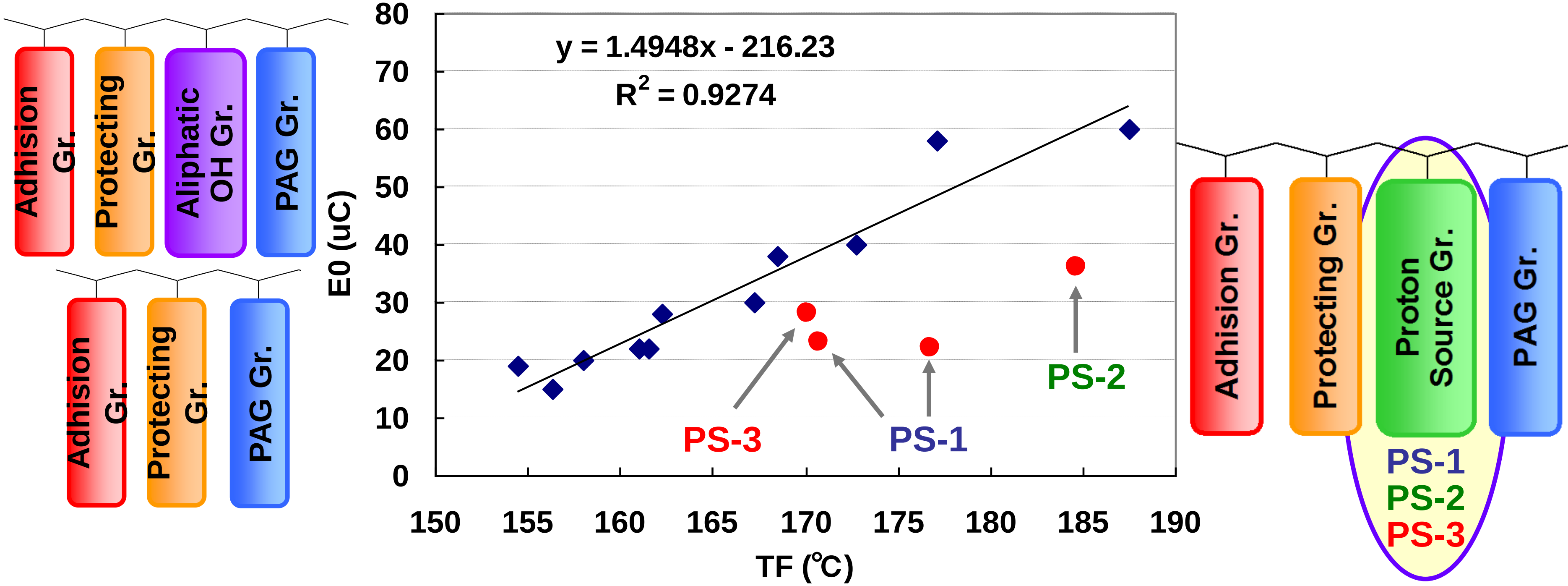
Coating & PAB → KrF exposure → PEB → Development → **Post bake**

- **C.D. shrink of 170nm iso hole pattern was observed with increasing Post bake temperature.**
- **TF temperature is determined as the point at which 10% C.D. shrink from original pattern is observed.**



Polymer Bound PAG with Proton Source
- thermal flow temperature and EB sensitivity -

- **TF temperature vs E0 sensitivity @EB exposure**



- **Blue plots : Linear relationship was seen between TF temperature and EB sensitivity.**
- **Red plots : Red plots related to the samples including PS unit show faster sensitivity than those of blue plots at the similar TF region regardless of higher TF temperature**
- **This would be because of effectiveness of proton source**

Polymer Bound PAG with Proton Source

- Albany MET result with Quadrupole illumination -

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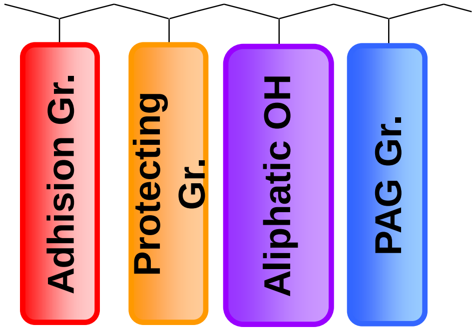


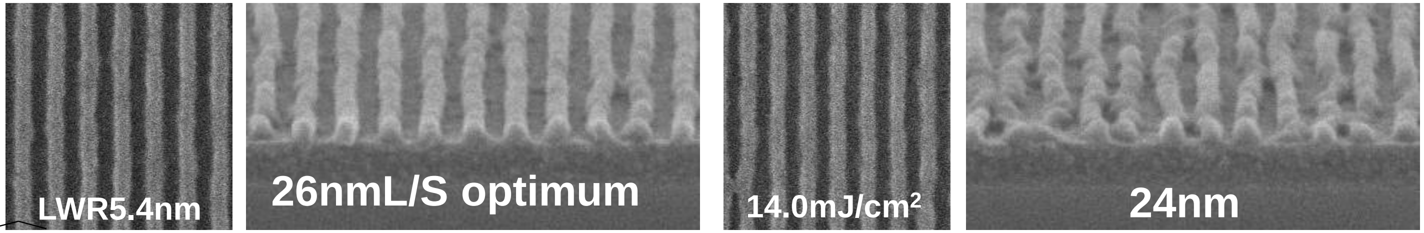
- **Lithographic performance was improved by attaching PAG unit into the polymer and modifying suitable proton source unit.**

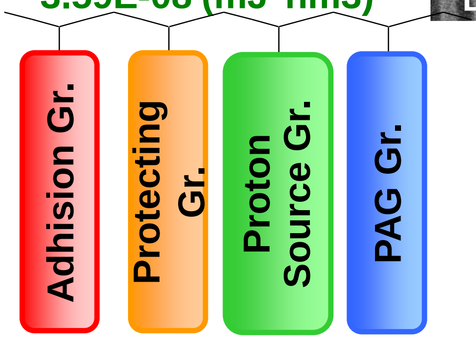
PBP Control

Eop: 14.0mJ/cm2
LWR:5.4nm
Z-factor
3.59E-08 (mJ·nm3)

26nmL/S

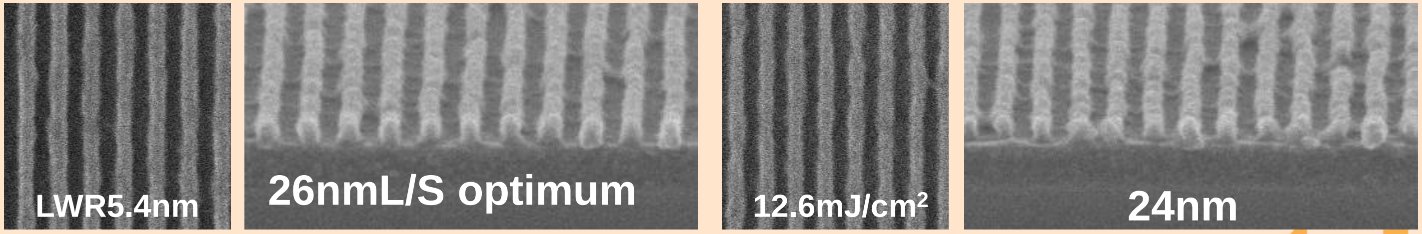
24nmL/S





PBP w/ PS-1

Eop: 12.6mJ/cm2
LWR:5.4nm
Z-factor
3.23E-08 (mJ·nm3)



Polymer Bound PAG with Proton Source

- Albany MET result with Quadrupole illumination -

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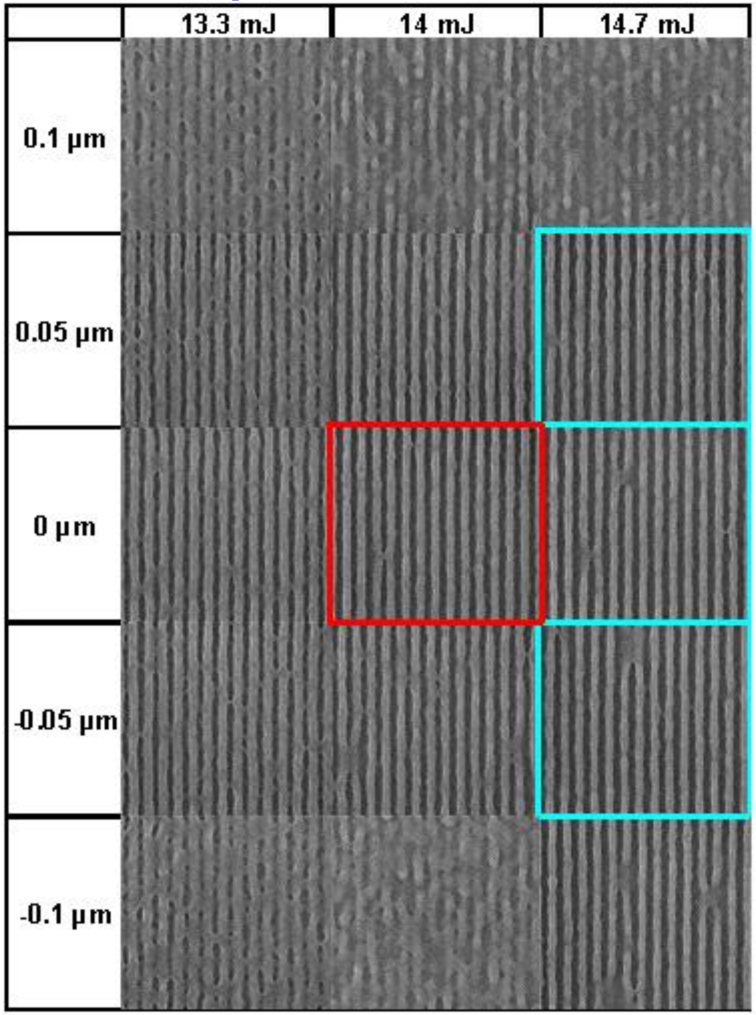
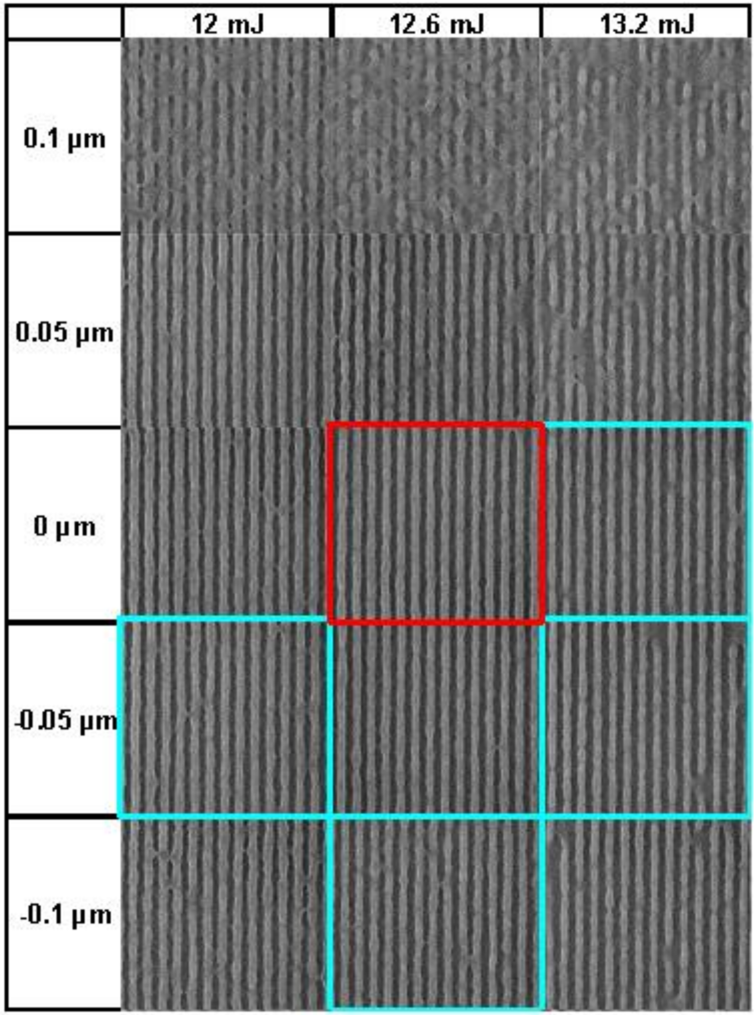
PBP Control

26nm L/S Eop: 14.0mJ/cm²



PBP w/ PS-1

26nm L/S Eop: 12.6mJ/cm²



- **PBP w/ PS-1 has wider PW at 24nm L/S.**

Summary

- **Effectivity of proton source unit was confirmed**
  - ✓ **From the acid amount experiment, higher acid amount was observed by using of PS-1**
  - ✓ **From the result of EB prescreening, Faster sensitivity is confirmed for PS-1 unit**
  - ✓ **PS-1 unit showed also faster sensitivity at EUV evaluation**
- **Resist Tg also affects to the resist sensitivity**
  - ✓ **TF temperature is related to E0 sensitivity**
  - ✓ **Deviation from TF-E0 relationship is observed for the samples including proton source unit in Polymer bound PAG platform**

- **Combination of proton source unit and polymer bound PAG would push resist performance further for overcoming RLS-trade-off relationship beyond 22nm HP**